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A Heterogeneous Tungsten Catalyst for Epoxidation of Terpenes and Tungsten-Catalyzed Synthesis of Acid-Sensitive Terpene Epoxides

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Introduction

Terpenes are cheap and often chiral precursors to fragrances, flavors, drugs, and agrochemicals.[1] Oxyfunctionalization of terpenes frequently starts with a selective epoxidation.[2] Although catalytic epoxidation is nowadays dominant for many commodities and fine chemicals, the synthesis of the major terpene epoxide, α-pinene oxide, still employs the stoichiometric peracid route.[3,4] In designing a catalytic alternative, H_2O_2 is the preferred reagent, but the choice of a (metal) catalyst is less evident, particularly if a convenient catalyst separation and product workup are desired or if one aims at the formation of acid-labile epoxides. Most of the reported tungsten catalysis is homogeneous and liquid biphasic, with a quaternary ammonium compound enhancing phase transfer of the peroxo W compound from the aqueous to the organic layer.[5−10]

We here report a heterogeneous, reusable W catalyst for the selective epoxidation of a series of terpene olefins. An essential step in the preparation of this solid catalyst is the ion exchange of a preformed peroxo PW-anion onto a resin in the presence of H_2O_2. Moreover, by careful choice of reaction conditions, phosphorus, and quaternary ammonium additives, we have designed a homogeneous W-based catalytic procedure for the production of labile epoxides. This is particularly interesting, as W-catalyzed epoxidation of α-pinene was till now an unresolved challenge.

Results and Discussion

A Heterogeneous Phosphotungstate Catalyst for Terpene Epoxidation. Epoxidations with H_2O_2 would be much facilitated if a heterogeneous catalyst were available that could handle even bulky substrates. However, known solid oxidation catalysts such as the molecular sieve Ti Silicalite-1 (TS-1) not only increase the acidity of aqueous H_2O_2; their small pore diameter also limits the access to the active sites for fairly large substrates.[11] In the reactions of Table 1, a heterogeneous catalyst is used that was obtained by exchange of a commercial, macroreticular Amberlite IRA-900 with the Venturello anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$.[5c] In the catalyst preparation, the resin was first converted into its NO_3^- form, as co-exchanged Cl^- appeared to decrease the selectivity of the epoxidation. Next, a solution of preformed $PW_4O_{24}[(C_4H_9)_4N]_3$ was shaken with the Amberlite, and H_2O_2 was added during this exchange to keep the peroxo W complexes intact.[7] The solid (PW−Amb) was thoroughly washed to remove nonexchanged peroxo PW quaternary ammonium compounds. As 40% or less of the anion exchange capacity (4.2 mequiv g^{-1}) is occupied by the PW-anions, the heterogeneity of the catalyst is guaranteed, particularly in organic solvents.

In the reactions of Table 1, typically 7−10 g of the desired product is obtained per gram of PW−Amb catalyst, or 80 mol of product per mole of exchanged $PW_4O_{24}^{3-}$. Note that TS-1 produces at most 4 g of epoxide per gram of catalyst with 1-hexene or 1-octene as a substrate before it is largely deactivated; the activity of larger pore Ti molecular sieves such as Ti-MCM-41 is even lower.[11] This high productivity of PW−Amb is coupled to a selectivity for epoxides that exceeds 90% for limonene (**2**), for unsaturated C_{10} alcohols or their esters (**3**−**5**, **7**−**9**), and for 3-carene (**12**) (entries 1−5, 7, 9, 11, and 12). Acetonitrile is a suitable solvent, but acetone may be used as well. In methanol yields are much lower. At longer reaction times and with more peroxide, diepoxides are easily formed, e.g., from **7** and **8** (entries 8 and 10).

The water-soluble substrate crotyl alcohol (**13**) is converted with excellent selectivity to its epoxide, even if all reagents are present in a single liquid phase (Table 1, entry 14). This is unusual for PW epoxidations, in which partition of the epoxide product to an apolar organic layer is generally desired to prevent hydrolysis in the acid aqueous layer.[5,6,9] Hence, while most two-phase W oxidations have been performed with olefins containing six or more carbon atoms, the single liquid-phase oxidation with PW−Amb is clearly not subjected to this limitation.

Conversion of unsaturated esters such as **7** and **8** proceeds optimally at 311 K, while subambient temperature is most suitable for the corresponding alcohols. In geraniol (**3**) and nerol (**4**), oxidation of the alcohol function represents about 5% of the products (Table 1, entries 3 and 4). Even with a secondary enol such as 2-cyclohexen-1-ol (**6**), the epoxidation still dominates over ketonization, with a 71% epoxide selectivity (Table 1, entry 6). This is noteworthy, as tungstate catalysts or phosphotungstate associations have been documented to effect ketonization of particularly secondary alcohols with H_2O_2, for instance,

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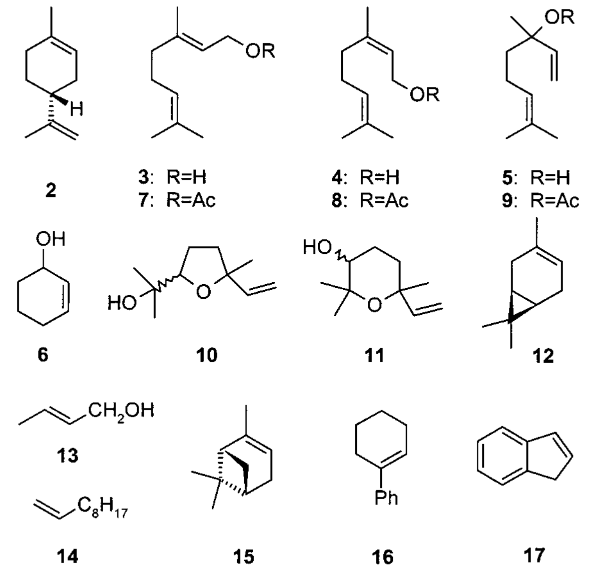
Table 1. Epoxidation of Monoterpenes and Crotyl Alcohol with H_2O_2 and the Heterogeneous PW−Amberlite Catalyst[a]

entry	substrate	*T*, °C (*t*, h)	olefin conversion (%)	epoxide selectivity (%)	product distribution (%)
1	limonene (**2**)	38 (24)	84	93	monoepoxide (85),[b] diepoxide (8)
2[c]	**2**	38 (24)	82	92	
3	geraniol (**3**)	0 (24)	74	94	monoepoxide (84),[d] diepoxide (10), geranial (6)
4	nerol (**4**)	0 (24)	71	95	monoepoxide (81),[e] diepoxide (14), neral (4)
5	linalool (**5**)	38 (40)	100	1	monoepoxide (1), **10** + **11** (96)[f]
6	2-cyclohexen-1-ol (**6**)	0 (40)	48	76	epoxy-ol (71),[g] enone (12), epoxy-one (5)
7	geranyl acetate (**7**)	38 (40)	94	92	monoepoxide (70),[h] diepoxide (22)
8[i]	**7**	38 (72)	99	84	monoepoxide (25), diepoxide (59)
9	neryl acetate (**8**)	38 (24)	90	92	monoepoxide (68),[j] diepoxide (24)
10[i]	**8**	38 (72)	99	76	monoepoxide (15), diepoxide (61)
11	linalyl acetate (**9**)	38 (24)	90	96	6,7-monoepoxide (94)[k]
12	3-carene (**12**)	38 (24)	55	97	*trans* epoxide (97)
13[c]	**12**	38 (24)	56	97	
14	crotyl alcohol (**13**)	38 (24)	82	99	*trans*:*cis* epoxide = 16 [l]

[a] Procedure: 1 mmol of olefin, 2 mmol of H_2O_2, 20 mg of catalyst, 1.5−4 mL CH_3CN. [b] 1,2:8,9 epoxide = 30, *cis*(1,2):*trans*(1,2) epoxide = 1.15. [c] Run with a reused catalyst. [d] 2,3:6,7 epoxide = 9.4. [e] 2,3:6,7 epoxide = 6.6. [f] Five rings:six rings = 2.3. [g] *syn*:*anti* = 1.8. [h] 6,7:2,3 epoxide = 31. [i] 4 mmol of H_2O_2. [j] 6,7:2,3 epoxide = 22. [k] 6,7:1,2 epoxide = 49. [l] Commercial crotyl alcohol contains 95% *trans* isomer.

Chart 1



in the reaction of carveol.[12] In our hands, the recent W-based epoxidation protocol of Sato et al.[9a] leads from **6** to 2-cyclohexen-1-one as the major product (68% enone selectivity; Table 2, entry 2).

The typical properties of W catalysis, such as stereospecificity, are well preserved in the heterogeneous catalyst. Thus, **4** gives the *cis*-2,3-epoxy-ol but not the trans product (2,3-epoxygeraniol). There are indications that in the oxidation of enols over PW−Amb, the directing effect of the hydroxyl group on the epoxidation is less decisive than for other W-catalyzed reactions. Thus, from **6**, the syn and anti epoxides are obtained in a 1.8 to 1 ratio (Table 1, entry 6), while this ratio is generally higher for homogeneous W catalysts (6 to 1; Table 2, entry 2). Analogous effects can be observed in the regioselectivity of the epoxidation of **3**. While alcohol coordination on W usually directs the epoxidation largely to the 2,3-bond, the 6,7-bond is now less disfavored for epoxidation, and this leads to doubly epoxidized products. Summarizing, the embedding of the PW-anion in the polymeric host not only provides heterogenization but also induces subtle changes in regio- and stereoselectivity.

After simple filtration of the macroreticular catalyst beads, the filtrate contains, apart from the solvent, the reaction product as sole organic component. While in typical homogeneous reactions the product must be distilled to separate it from quaternary N phase transfer catalysts or from byproducts of the peracid, this step can be avoided with the heterogeneous catalyst. Catalyst reusability was tested for several substrates and proved satisfactory with respect to conversion and selectivity in all cases. Data for a second run with **2** or **12** and a recuperated PW−Amb catalyst are included in Table 1 (entries 2 and 13). The advantages of the heterogeneous reaction are particularly well illustrated in the oxidation of linalool (**5**). In this reaction, the 6,7-epoxide directly rearranges to a mixture of the diastereomeric five- and six-ring tetrahydrofurans and pyrans (**10**, **11**), with an overall yield of 96% (Table 1, entry 5). Exactly the same product composition, termed linalool oxide, is obtained with a stoichiometric peracid.[1]

Preparation of Acid-Sensitive Terpene Epoxides with Tungsten Catalysts. As activation of aqueous H_2O_2 is often based on the Lewis acidity of the catalysts, there are only a few catalysts that operate in inherently neutral conditions.[3] Manganese catalysts do not cause epoxide solvolysis but face other drawbacks, e.g., pronounced steric hindrance at the active site, which makes them less suitable for reactions with trisubstituted olefins such as α-pinene (**15**).[13] With a catalytic amount of CH_3ReO_3 and H_2O_2, **15** is epoxidized selectively, but buffering of the Lewis acidity requires up to equimolar amounts of pyridine or bipyridine, which are largely consumed with formation of the corresponding N-oxides.[14] Typical W procedures from literature do not allow prevention of hydrolysis or rearrangement of the epoxides. For in-

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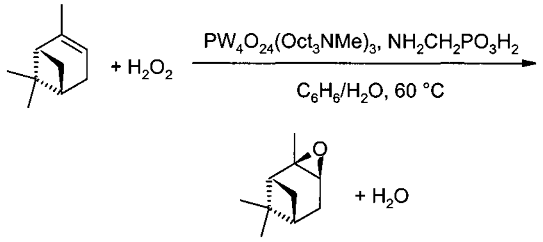
Table 2. Homogeneous Catalytic Synthesis of (Acid-Aensitive) Epoxides with the Venturello Complex 1 and (Aminomethyl)phosphonic Acid as the Co-catalyst[a]

entry	substrate	mole % vs olefin $NH_2CH_2PO_3H_2$	**1**	Na_2WO_4	*T*, °C (*t*, h)	olefin conversion (%)	epoxide selectivity (%)	comments
1	1-decene (**14**)	1	0	2.5	90 (4)	99	90	
2	2-cyclohexen-1-ol (**6**)	1	0	2.5	60 (4)	57	24	epoxy-ol (24%),[b] enone (68%)
3	α-pinene (**15**)	1	0	2.5	90 (4)	29	0	diol (43%), campholenic aldehyde (10%), other rearrangement products
4	α-pinene (**15**)	2	2	0	60 (2)	83	92[c]	
5	**15**	2	1	3	60 (1)	83	91	
6	**15**	2	1.7	0	60 (1)	100	53	no pH control (pH = 2.1)
7	**15**	0	1	3	60 (1)	43	93	no extra P source
8	**15**	2	1	2.6	60 (1)	42	88	P-source = H_3PO_4
9	**15**	2	1.6	0	60 (2.5)	95	72	P-source = ethanolamine phosphate
10	**15**	2	0	7	60 (2)	17	90	no preformed catalyst
11	**15**	0.6	0.3	0.8	60 (1)	40	87	0.6 equiv H_2O_2
12	**15**	2	1	2.7	60 (2)	92	85	solvent: toluene
13	3-carene (**12**)	1	1	2	60 (4)	97	97	*trans* epoxide
14	linalool (**5**)	9	3.7	11	60 (4)	85	68	6,7-monoepoxide
15	1-phenyl-1-cyclohexene (**16**)	6	2.6	7	60 (4)	97	83	$pH_{aq} = 5$
16	indene (**17**)	7	2.5	7	60 (4)	96	68	$pH_{aq} = 5$

[a] Procedures: Entries 1−3: according to ref 9a: 1 equiv olefin, 1.5 equiv aqueous 35% H_2O_2, 0.01 equiv $[(C_8H_{17})_3NCH_3]HSO_4$; $NH_2CH_2PO_3H_2$, and $Na_2WO_4{\cdot}2H_2O$ as indicated (mol % of olefin); 0.6 mL toluene per mmole substrate. No pH control. (entries 4−16): 1 equiv olefin, 2 equiv aqueous 35% H_2O_2; P compound ($NH_2CH_2PO_3H_2$, except for entries 7−9), **1** = $PW_4O_{24}[(C_8H_{17})_3NCH_3]_3$ and $Na_2WO_4{\cdot}2H_2O$ as indicated (mol %); 1 mL benzene per mmole substrate. pH was brought to 4.2 ± 0.2 with aqueous NaOH (except in entries 6, 15, 16). In entry 10, 3 mole % $[(C_8H_{17})_3NCH_3]Cl$ was added as a phase transfer catalyst. [b] *syn*:*anti* = 6. [c] 99% of the α-pinene oxide is *trans*.

stance, while in the 1-decene (**14**) epoxidation the yield reported by Sato et al.[9] is satisfactorily reproduced (90%; Table 2, entry 1), the same procedure leads to essentially zero epoxide yield with **15** (entry 3). Characteristically, in previous reports on W- or PW-catalyzed synthesis of labile or terpene-derived epoxides, the reaction of α-pinene is not addressed.[5b,6b,10]

However, our data show that in appropriate conditions **15** can be epoxidized with W, with 92% selectivity at over 80% olefin conversion (eq 1). Table 2 contains some of the essential steps in the optimization of the reaction. The best results are obtained when P and W are preassociated in a Venturello complex ($PW_4O_{24}[(C_8H_{17})_3NCH_3]_3$), which also contains the quaternary ammonium phase transfer agent (entry 4). Part of the W may be introduced as the disodium salt into the aqueous phase without major effects on the reaction (entry 5). Adjusting the pH of the aqueous phase to 4.2 with aqueous NaOH somewhat lowers the reaction rate but has a large positive impact on the selectivity (entry 6). The addition of the extra P source (aminomethyl)phosphonic acid induces a clear rate acceleration, combined with an excellent epoxide selectivity (compare entries 5 and 7). This effect is not observed when phosphoric acid is used as the P source, even if in both cases the pH is adjusted to 4.2 (entry 8). Better results are obtained with other organic P compounds, such as ethanolamine phosphate (entry 9).



83 % conversion, 92 % selectivity

When tungstate, the salt of the quaternary ammonium component (Aliquat 336) and the phosphorus compound are mixed in situ, activities are much lower (entry 10). The optimized reaction can be conducted with excess H_2O_2, leading to almost complete conversion, or with an understoichiometric amount of peroxide, with recovery of the remaining **15** (entries 4 and 11). In both cases, the epoxide selectivity is around 85−90%. This is remarkable, as in Venturello's original procedure excess olefin is necessary to preserve high epoxide selectivity.[5b] In our experience, 1 mL of solvent is required per mmole of substrate to favor partition of the epoxide to the organic phase; instead of halocarbon solvents, benzene and even toluene give excellent results (entry 12).

Our method was successfully expanded to other terpene substrates such as **12** (94% yield on olefin charged) (entry 13). For **5**, the intramolecular cyclization can largely be prevented, and the 6,7-epoxide is the major product (68% yield on olefin reacted) (entry 14). Nonterpene substrates with sensitive epoxides are also suitable starting products; for instance, in reactions with an aqueous layer at pH 5, 1-phenyl-1-cyclohexene (**16**) and indene (**17**) were converted into the epoxide products as evidenced by NMR (entries 15 and 16).

Conclusion

We have explored and widened the scope of tungsten catalysis for epoxidation of terpenoid and related olefins. A heterogeneous catalyst is now available for most substrates with reasonably stable epoxides. The catalyst can be used in small concentrations and facilitates product workup. Moreover, we report the first W-catalyzed epoxidation of α-pinene, in a biphasic reaction with a buffered aqueous layer. The use of (aminomethyl)phosphonic acid as a cocatalyst is beneficial for the reaction rate while keeping the epoxide selectivity high. For heterogeneous and for homogeneous catalysis, it is advantageous to employ preformed peroxo PW-anions.

Experimental Section

Materials. All commercial products were of the highest grade available and were used as such. Hydrogen peroxide was a 35% aqueous solution (Akros) or a 50% solution (Rectapur). The

Venturello complexes $PW_4O_{24}[(C_4H_9)_4N]_3$ and $PW_4O_{24}[(C_8H_{17})_3NCH_3]_3$ were prepared as described in the literature.[5b,c] A reported procedure was also followed for preparation of the phase transfer agent $[(C_8H_{17})_3NCH_3]HSO_4$.[9b]

Preparation of the Heterogeneous Catalyst PW−Amb. Amberlite IRA 900 (anion exchange capacity, 4.2 mequiv per g dry weight) was converted into its NO_3^- form in a 0.2 M $NaNO_3$ solution and dried. One gram of $PW_4O_{24}[(C_4H_9)_4N]_3$ was dissolved in 6 mL of acetone and 2 mL of 35% H_2O_2, and 0.8 g of the Amberlite was added to this solution. Ion exchange was performed by shaking at room temperature. After 16 h, the solid was filtered; washed with water, water−acetone (50−50), and acetone; and eventually air-dried.

Epoxidation Procedures. (1) With the Heterogeneous PW−Amb Catalyst (Table 1). A 20 mg portion of catalyst is suspended in a solution of 1 mmol of olefin in 1.5−4 mL of CH_3CN, and 50% H_2O_2 (2 mmol) is added. The mixture is stirred at 0 or 38 °C. After reaction, the catalyst beads are filtered, CH_3CN is evaporated, and EtOEt is added. Evaporation of the organic layer leads to the isolated product.

(2) Liquid Biphasic Epoxidation (Table 2, entries 1−3), e.g., of **14**. $Na_2WO_4{\cdot}2H_2O$, $NH_2CH_2PO_3H_2$, aqueous 35% H_2O_2, and $[(C_8H_{17})_3NCH_3]HSO_4$ are mixed in a 0.025:0.01:1.50:0.01 ratio. After vigorous stirring for 15 min at room temperature, the olefin (1 equiv) diluted in toluene (0.6 mL per mmole of substrate) is added. Reaction is conducted for 4 h at 60−90 °C (750 rpm).

(3) Synthesis of Acid-Sensitive Terpene Epoxides (e.g., α-pinene epoxide; Table 2, entry 5). An aqueous mixture of 35% H_2O_2, $NH_2CH_2PO_3H_2$, $PW_4O_{24}[(C_8H_{17})_3NCH_3]_3$, and $Na_2WO_4{\cdot}2H_2O$ (molar ratio 2:0.02:0.01:0.03) is brought to pH 4.2 with 0.5 N NaOH. This mixture is then added to the olefin (1 equiv) dissolved in the solvent (1 mL of benzene per mmole of olefin). The reaction mixture is stirred at 500 rpm and 60 °C. After reaction, the organic layer is washed with a phosphate buffer and with 10% aqueous Na_2SO_3 to decompose unreacted H_2O_2. Cooling in a freezer (e.g., for 3 h at −20 °C) causes precipitation of most of the quaternary ammonium compound, and after solvent evaporation the product is ready for NMR analysis. For other entries in Table 2 (e.g., 13−16), the procedure was modified as indicated in Table 2.

Product analysis was done with a GLC (50 m Chrompack CP−Sil 5 column). In GLC calculations, all peaks amounting to at least 0.3% of the total products were taken into account, making the analysis much more precise than even a routine NMR determination. Identity of epoxide products was confirmed by 300 MHz ^1H and ^{13}C NMR. Spectra were compared with those of authentic compounds for linalool oxide, *cis*- and *trans*-1,2-limonene oxide, and α-pinene oxide. Listed data (^1H and/or ^{13}C) are available for α-pinene oxide,[15] 1,2-limonene oxide,[15,16] 3-carene oxide,[16] 1,2-epoxyindane,[17] 6,7-epoxylinalyl acetate,[18] 6,7-epoxygeranyl acetate,[18] 6,7-epoxyneryl acetate,[18] 2,3-epoxygeraniol,[19] and 2,3-epoxynerol.[20,21]

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Supporting Information Available: Physical data of the products. This material is available free of charge via the Internet at http://pubs.acs.org. This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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